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(54) Title: PROCESS FOR DEPOSITING CONDUCTING LAYER ON SUBSTRATE

(57) Abstract

A process for forming a conductive layer on a substrate, comprising the steps of depositing ink on the substrate by means of lithographic printing to form a seeding layer, and depositing a first electrically conducting layer on the seeding layer by electroless deposition.

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PROCESS FOR DEPOSITING CONDUCTING LAYER ON SUBSTRATE

The present invention relates to a process for forming an electrically conductive layer on a substrate, and in particular to a process for forming such a layer on a substrate which can be used as a circuit board in an electrical assembly.

Conventionally, silicon devices are mounted on printed circuit boards (PCB). A printed circuit board generally consists of etched copper on glass fiber laminate, tin plated and possibly carrying further layers of lacquer for protection and labeling. Many operations of cropping, drilling, etching and plating are involved in its preparation. It is not cheap, and the production processes can have significant environmental impact.

The two major environment hazards posed by PCB manufacture are the waste effluent which is acidic and contains heavy metals (especially copper), and the use of hydrocarbons in photoresist developer and stripper. Stricter pollution limits imposed by water authorities are one driving force to reduce copper in effluent. In theory, waste effluent could be eliminated by a totally additive process for copper deposition, which would also offer considerable cost savings, but a satisfactory process has not yet been developed.

Attempts to avoid the use of a circuit board as such include the use of both thick and thin film techniques, normally associated with higher cost, not lower. Resistors are formed on a ceramic substrate by depositing tracks of a suitable film, sometimes trimmed to precise values by laser etching. A film of higher conductivity is generally used for interconnection.

WO 97/48257, which has common applicants with the present application, the disclosure of which is incorporated herein, discloses an alternative method of forming an electrical circuit board, whereby a conducting ink is lithographically printed onto a substrate in order to form an electrical circuit. The ink comprises electrically

conductive particles (such as metallic silver) suspended in an organic resin such as an alkyd resin. The manufacture of electrical components such as resistors, capacitors and antennae is also described.

Although the circuit printing technique disclosed in WO 97/48257 is a significant improvement on previous techniques, it has a number of disadvantages.

First, it is advantageous to electroplate a second conducting layer onto the conductive ink disclosed in WO 97/48257 in order that electrical components can then be soldered on to the substrate and/or to reduce the resistivity of the circuit. The problem is that the ink does not adhere sufficiently well to the substrate to enable electroplating.

Second, in order to prepare a conductive ink, it is necessary to employ particulate conductive material with a particulate surface treatment (e.g. a coating of a long chain fatty acid) to enable the particles to be dispersed in the resin in such a manner as to render the dried ink electrically conductive. However, this surface treatment precludes further treatment of the dried ink, for example it prevents deposition of a further conductive layer by electroless deposition.

Third, it is difficult to solder electrical components onto an electrical circuit formed from conductive ink layers, because the layers do not contain sufficiently a high metal loading to create a suitable solder join. This means that components must be affixed using conductive polymer adhesive or a mechanical joint. However, it is thought that these joining methods do not age as well as solder, and exhibit higher electrical resistance. Moreover, any increase in the content of conductive particles in the ink is to the detriment of the ink's rheological properties.

According to a first aspect of the present invention, there is provided a process for forming a conductive layer on the substrate, comprising the steps of depositing ink on

the substrate by means of lithographic printing to form a seeding layer, and depositing a first electrically conducting layer on the seeding layer by electroless deposition.

Electroless deposition (or plating) is a well-known technique which involves coating an object (or part of an object) by means of a chemical reduction process, which, once initiated, is also-catalytic. The process is similar to electroplating except that no external current is required. In order to electroless plate an object, a seeding layer of suitable geometry and electrical and chemical characteristics must be formed on the object in order to provide nucleation sites for the metal to be deposited. It is thought that the seeding layer acts as a catalyst, in that it reduces the activation energy for the deposition step.

The term "lithographic printing" referred to herein is a printing process which utilizes differences in surface chemistry of the printing plate, including hydrophilic and hydrophobic properties. It does not refer to the commonly used process involving photoresist and etching occurring during the production of etched circuit boards and/or silicon semiconductor micro electronics. The term "ink" is intended to mean any material suitable for printing.

The ink which is employed in the present invention preferably comprises a particulate material suspended in a mixture of a resin and an organic solvent. Most preferably, the particulate material is particulate metal or carbon. Particularly suitable materials include silver, gold, copper, zinc or nickel. The particle size may be from 0.1 to 10 micrometers, and preferably from 0.25 to 1 micrometers, more preferably greater than 0.1 micrometers and less than (but not equal to) 1 micrometer, and most preferably from 0.25 to 0.75 micrometers.

The amount of the particulate material in the ink is preferably from 50 to 90% w/w, and most preferably about 75% w/w.

The resin for use in the ink may be a polymer blended with various oils. Preferably, the resin comprises a polymer having amide groups, for example a nylon-based polymer.

One resin which has been found to be particularly suitable is available commercially Lawter International (of Ketenislaan 1c-Haven 1520, B-9130 Kallow, Belgium) under the trade name "Nypol 3". Nypol 3 comprises a modified polyamide and tung oil and vegetable oil blends.

Other resins which have exhibited acceptable performance include phenolic modified resin and alkyd resins, which are blended with modified mineral oils and vegetable oils.

In order to form the ink, the resin is mixed with a solvent and a suspension of the particulate material is formed. The solvent (or diluent) can be any suitable organic solvent with a boiling point of about 250°C.

The substrate onto which the conductive layer is printed is preferably formed from a polymer, and preferably comprises a flexible sheet. Suitable polymers include polyethylene, polypropylene, a polyester, a polyamide, a polyimide or a polysulphone. The substrate may be treated to improve adhesion of the ink to the substrate surface. For example, the substrate may be coated with a copolymer adhesive layer, or the surface may be chemically treated or subjected to corona treatment.

Preferably, the substrate is formed from a polyester, polyethylene, polypropylene or a polyamide, with or without a copolymer adhesive layer. In a particularly preferred embodiment, the substrate is a copolymer coated polyester, such as that available commercially from GBC (UK) Ltd of Rutherford Road, Basingstoke, Hampshire, RG24 8PD.

It has been discovered that modified polyamide resins work acceptably well with substrates formed from polyethylene, polypropylene, polyamide and polysulphone. Modified phenolic resins work acceptably well with polyester, polyimide or polysulphone substrates. Alkyd resins adhere reasonable well to polyester substrates.

As described above, the ink is deposited onto a substrate by means of a lithographic printing process in order to form a seeding layer for electroless deposition. The thickness of the seeding layer in the present invention is preferably from 3 to 5 micrometers.

Electroless deposition of a first electrically conductive layer is carried out by conventional means. The conducting layer may be formed from any suitable electrically conductive material which can be deposited by electroless deposition, for example copper, silver, nickel or gold.

The thickness of the first conducting layer may be up to 4 micrometers and is preferably about 1 micrometer (although the thickness will be determined by the required electrical specifications).

The process of the present invention may comprise the step of electroplating a second electrically conducting layer onto the first conducting layer.

Electroplating is a well-known method whereby an object or part of an object is coated by means of electrolytic deposition. In order to be electroplated, the object has to have an electrode which exhibits a suitable geometry and electrical and chemical characteristics. In the case of the present invention, the first conducting layer which is deposited on the seed layer acts as an electrode in the electroplating process, thereby enabling the second conducting layer to be electrolytically deposited onto the first conducting layer.

The addition of a second conducting layer improves the conductivity of the circuit tracks and improves the soldering of electrical components directly onto the substrate in order to form electrical assemblies (components may be soldered directly onto the first conducting layer).

If a second layer is going to be electroplated onto the first, then the first layer does not need to be as much as 1 micrometer thick; a thickness which render the substrate conductive is required, for example from 0.25 to 0.5 μm.

As with the first conducting layer, the second layer may comprise any suitable electrically conducting material which can be electroplated. The thickness of the second conducting layer may be anything up to 35 micrometers, depending on the required specification of the circuit board.

Although a conducting layer can be electroplated onto an electrical circuit prepared according to the process disclosed in WO 97/48257, the resulting circuit board is structurally unstable due to the poor adhesion of the conducting ink onto the substrate.

By contrast, an electrical component can be soldered directly onto an electrical circuit prepared by the present method, particularly if a second conducting layer is deposited by means of the electroplating step, since by this step sufficient conducting layer can be deposited to which a good solder link can be formed.

One example application of the present invention is in the manufacture of electronic circuit boards. The lithographically deposited seeding layer is printed in the graphical configuration of an electrical or electronic circuit. The seeding layer can then be electrolessly plated with copper and a further layer of tin or other protective layer. These layers improve the conductivity of the circuit tracks and allow them to be soldered directly onto via existing solder technologies.

The lithographic process of production of seeding layers offers advantages of speed of production and very fine track and gap width resolution.

An embodiment of the present invention is below, by way of illustration only. For ease of understanding, the embodiment is described by way of its component parts.

The ink

Ink layers deposited by the preferred lithographic printing process are about 5 micrometers (5×10^{-6}m) thick. This may be compared to about 25 micrometers for conductive layers deposited by screen printing, and 20-75 micrometers of copper typically laminated onto a conventional printed circuit board.

The adopted approach has been to formulate an ink from particles suspended in an organic resin. Manipulation of the resin formulation permits a degree of control over certain mechanical characteristics of the ink (e.g. viscosity).

As described above, the particulate material should be such as to enable the electroless deposition step. Suitable materials include silver, copper, carbon and palladium.

Hydrocarbon solvents and other suitable additives are used to adjust the printing, wear resistance and drying properties of the printed layer. An antioxidant (such as eugenol) is preferably incorporated to react with free radicals and thereby prevent auto-oxidation of the resin. In other words, the antioxidant prevents the resin from drying too quickly.

A drying agent such as a cobalt salt can be included to dry the resin once the antioxidant is used up.

An example of a preferred formulation of an ink is:

Component	Identity	Amount
Particulate	Silver particles with a mean particle size of 1 micrometer	about 75% w/w
Resin	Nylon based hydrocarbon	about 23% w/w
Solvent	Medium to high boiling point organic	about 2% w/w
Drying agent	Cobalt salt	trace
Antioxidant	Eugenol	trace

The resulting ink formulation exhibits Newtonian properties, exhibiting a viscosity of about 5^4 to 10^4mPaS @ 25 degrees C. Suitable viscosities of ink formulations are considered to lie in the range 10^3mPaS @ 25 degrees C to 10^5mPaS @ 25°C.

The substrate

The copolymer-coated polyester from GBC (UK) Ltd was used.

Printing process

First, the required artwork (that is, the pattern which is to become the electrical circuit) is applied to an anodised aluminium plate using the standard photoresist method used in the lithographic printing process. Second, the aluminium plate is used as a template in a lithographic process to apply the ink to the substrate in the required artwork pattern.

Electroless plating

The electroless process involves placing the inked substrate in an electroless bath (such as the bath supplied by Shipley Ronal Limited) which contains a commercially available electroless plating solution. This comprises a solution of a copper salt (such as copper sulphate); a chelating agent e.g. EDTA; stabilisers such as sulphur compounds or heavy metals; an aqueous alkaline solution, for example aqueous

sodium hydroxide; a reducing agent for example formaldehyde; and, optionally, a surfactant. This is known under the trade mark "CP78 process".

Typical deposition rates achievable by use of this commercial process are approximately 4 micrometers of metal per hour. Typically therefore for a 1 micrometer layer, the substrate is placed in the electroless bath for ten to fifteen minutes.

As mentioned above, if the substrate is subsequently to be electroplated, then it is not necessary to electroless deposit a 1 micrometer layer. A sufficiently thick layer to act as an electrode in the electroplating process will result from placing the substrate in the electroless bath for about three to seven minutes.

<u>Electroplating process</u>

Electroplating processes are well known in the art. For example, copper sulphate solution is used as the electrolyte. The rate of copper deposition is dependent upon the surface area of the cathode and the current density. A typical current density is 25 Amps per square decametre. The anode is copper and the cathode is the item to be plated (i.e. the conductive tracks).

<u>Manufacture of electrical circuit board</u>

As described above, electrical components can be soldered directly onto the conductive layers on substrate formed by the above processes. Alternatively, a conductive polymer adhesive can be used such as an epoxy adhesive.

The present process can be employed to form a variety of devices comprising electrical circuitry. Examples of electrical assemblies which can be created using the above processes include battery interconnect circuitry, microwave integrated circuits,

antennae, such as microwave antennae, planar antennae or contoured antennae structures.

In a further aspect of the present invention, there is provided a method of depositing an electrically conducting layer onto a conducting layer of a substrate prepared by the method disclosed in WO 97/48257 by means of electroplating, electroless deposition, or a combination thereof.

The disclosures in UK patent application numbers GB 9826446.8 and GB9826447.6, from which this application claims priority, and in the abstract accompanying this application, are incorporated herein by reference.

CLAIMS

1. A process for forming a conductive layer on a substrate, comprising the steps of depositing ink on the substrate by means of lithographic printing to form a seeding layer, and depositing a first electrically conducting layer on the seeding layer by electroless deposition.

2. A process as claimed in claim 1, comprising the step of electroplating a second electrically conducting layer onto the first electrically conducting layer.

3. A process as claimed in any preceding claim, wherein the substrate is formed from a polymer into a flexible sheet.

4. A process as claimed in any preceding claim, wherein the substrate is coated with a copolymer adhesive.

5. A process as claimed in any preceding claim, wherein the ink comprises a particulate material suspended in a mixture of a resin and an organic solvent.

6. A process as claimed in claim 5, wherein said material is a metal or carbon.

7. A process as claimed in claim 5 or 6, wherein the resin is a polymer having amide groups.

8. A process as claimed in any preceding claim, wherein the thickness of the seeding layer is from 3 to 5μm.

9. A process as claimed in any preceding claim, wherein the thickness of the first electrically conducting layer is up to 4μm.

10. A process as claimed in any preceding claim, wherein the thickness of the first electrically conducting layer is about 0.25μm.

11. A process as claimed in any preceding claim, wherein the first electrically conducting layer is formed from copper, palladium, silver, gold, platinum, nickel.

12. A process as claimed in any preceding claim, including the step of soldering an electrical component on the substrate.

13. A process as claimed in any of claims 1 to 11, including the step of attaching an electrical component to the first or second conducting layer by means of a conductive polymer adhesive.

14. A electrical assembly comprising a substrate having at least one electrically conducting layer, which layer has been formed by a process as claimed in any of claims 1 to 13.

15. A lithographic ink for use in a lithographic printing process onto a polymer substrate, the ink comprising a particulate material suspended in a mixture of a resin and an organic solvent, wherein the resin comprises a polyamide.

16. An ink as claimed in claim 15, wherein said material is a metal or carbon.

17. An interconnect for a battery which is formed by a process as claimed in any of claims 1 to 13.

18. A battery including an interconnect as claimed in claim 17.

INTERNATIONAL SEARCH REPORT

Intern   nal Application No
PCT/GB 99/04064

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H05K1/09

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H05K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 97 48257 A (EVANS PETER SIDNEY ALBERT ;UNIV BRUNEL (GB); HARRISON DAVID (GB);) 18 December 1997 (1997-12-18) cited in the application the whole document	1-18
Y	EP 0 664 664 A (IBM) 26 July 1995 (1995-07-26) claims 11-14	1-18

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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Information on patent family members

Intern ...al Application No
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Patent document cited in search report		Publication date	Patent family member(s)			Publication date
WO 9748257	A	18-12-1997	CA	2258108	A	18-12-1997
			EP	0910935	A	28-04-1999
EP 0664664	A	26-07-1995	US	5509557	A	23-04-1996
			JP	2643099	B	20-08-1997
			JP	7221443	A	18-08-1995